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Center: Consortium for Materials Development in Space
The University of Alabama in Hunstville (UAH)

Project Name: **"Physical Vapor Transport Crystal Growth"**

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Introduction

The goals of this research are two-fold, to study effective means of growing ZnSe crystals of good optical quality and to determine the advantages of growing such crystals in microgravity.

Single crystals of zinc selenide have numerous applications in optical devices[1] and consequently there is a demand for crystals of greater optical perfection. They are used as p-n junction light-emitting diodes,[2-6] laser windows, gradient index materials, photo-conductors, etc. When doped with sulfur, the compound ZnS_xSe_{1-x} is a blue emission material. Growth has been achieved under moderate pressure from the melt as well as from chemical and physical vapor deposition, and thin films have been made by evaporation and by epitaxial growth. The growth method used in this study is that of vapor transport and condensation within a sealed quartz ampoule. Physical vapor transport has the advantage of requiring lower temperatures than growth from the melt and it is less vulnerable to the severe strains that can result from growth at very high temperatures. Physical vapor transport is less complex than growth by chemical vapor transport since the latter method often involves a number of different molecular species, all of whose vapor pressures must be known as a function of temperature.

Boeing Aerospace Company (BAC) and the Consortium for Materials Development in Space (CMDS) expect to fly a joint experiment on the growth of zinc selenide crystals on STS-29, the fourth Shuttle flight after flights resume. In support of the flight system development program, investigators at BAC and UAH are currently concentrating their efforts upon the following four ground-based activities: (1) determination of the optimum growth conditions, (2) growth cartridge development, (3) ground science furnace development, and (4) development of requirements for the flight system. The past year's efforts toward achieving these goals are summarized below.

Crystal Growth

There are four basic steps to crystal growth by physical vapor transport, namely, vaporization of the constituent materials, transport of the vapor to the growth site, condensation of the vapor, and assimilation into the crystal structure. The last of these processes includes the thermally activated movement of adsorbed atoms or molecules about the surface of the crystal. The growth process normally takes place in a thermal gradient such that the condensation zone is 20 to 100°C cooler than the source materials. In a sealed ampoule vapor transport is driven by diffusion and by the difference in partial pressures at the source and the seed, as well as by convection. The actual growth rate is determined by the slowest of the above steps. Experience indicates that step 2, the transport of the vapor to the growth site, is generally the rate-limiting process.

In last year's Annual Report it was pointed out that our two major problems were (1) little or no vapor transport and (2) multiple nucleation sites, which, in extreme cases resulted in the formation of a polycrystalline coating on the ampoule wall. The principal factors affecting the vapor transport rate are the thermal profile of the furnace, the stoichiometry and purity of the starting materials, and the residual vapor pressure within the sealed ampoule. Careful pre-treatment of the starting materials is a major factor in enhancing both the stoichiometry and the purity of the materials, with the added benefit of reducing the residual vapor pressure within the ampoule after it is sealed off. Since the furnace had, on a few occasions, produced acceptable transport rates, it was reasonable to assume that the the thermal profile of the furnace was not a major problem. Therefore, it was conjectured that the low transport rates which were frequently obtained were caused by a combination of impurities and poor stoichiometry in the starting material, accompanied by excessively high residual vapor pressures in the ampoules. We then modified our pre-treatment and vacuum bakeout procedures and obtained greatly improved transport rates, as high as 160 mg per day. In the new procedure the ampoule is first cleaned with aqua regia and then rinsed with distilled water, followed by a rinse with methanol or acetone. It is then pumped down to 10^{-6} torr and baked at 1000°C for 2 hours. The ampoule is loaded with 2 to 3 grams of polycrystalline ZnSe obtained from material that had been previously transported. The sample is then refined further by baking at 550°C for two hours under a vacuum of 10^{-6} torr and then sealed off. Using these procedures we achieved the complete transport of all of the starting material in our most recent growth run.

The creation of nucleation sites is the result of the combined effects of the geometry of the ampoule and its cold finger, the position of the ampoule relative to the furnace profile, and the nature of the profile itself. In all early growth runs the transported material formed a polycrystalline cone on the wall of the ampoule at the growth end. Our experimental efforts to obtain single site growth were devoted to modifying the apex region of the ampoule where it joins the cold finger, and to altering the position of the ampoule in the thermal profile of the furnace. Figure 1 shows two stages in achieving better growth. In the upper picture single crystals of millimeter size emerge from the polycrystalline layer on the ampoule wall. In the lower picture there is no polycrystalline layer; instead, single crystals of millimeter size grew at discrete sites on the ampoule wall. Best results were obtained by extending the ampoule into a narrow tube in the cold finger as shown in Figures 3 and 4. Using this method several boules containing single crystals of nearly centimeter size were obtained without any material sticking to the ampoule walls. Photographs of these large crystals are shown in Figure 5.

As of this date the optimum conditions for crystal growth have not been determined. However, successful growth runs were made in both of the furnaces shown in Figures 2 and 3. Figure 2 shows the temperature profile for a Marshall furnace operating at a source temperature of 1000°C and a growth temperature of 975°C. A transport rate of 145 mg/day was obtained during a 10-day run. Figure 3 shows the profile for the single-zone BAC #0 furnace. With a source temperature of about 940°C and a temperature difference of about 60°C, a transport rate of 168 mg/day was obtained during a 15-day run. Five successful growth runs have been completed as shown in Table I. Four of these runs have produced the crystals shown in Figure 5. Four boules weighing 1.4 to 3 grams have been obtained to date. Each of these boules contains a relatively large

TABLE I

BOULE NUMBER	WEIGHT (Grams)	SOURCE/GROWTH TEMP (oC)	RUN TIME (DAYS)	AV.GROWTH RATE mg/day	FURNACE	TRANSPORT
2	1.44	1003/976	10	144	Marshall	Incomplete
3	2.52	940/880	15	168	Transparent	Incomplete
4	2.04	1003/976	20	102	Marshall	Incomplete
5	0.5	1003/976	22		Marshall	Incomplete
6	3	1003/976	32	100	Marshall	Complete

single crystal, although the boule as a whole is a composite of many crystallites. Three of these boules are shown in Figure 5.

Crystal Characterization

Crystals will be characterized during the next year by means of the following methods. First, they will be examined for their structural and compositional purity using x-ray diffraction, optical and electron microscopy and Raman spectroscopy. Secondly, they will be evaluated for applications in optical devices by such measurements as optical absorption, luminescence, photoconductivity, and the Hall effect.

Growth Cartridge Development

BAC has gained approval for the basic cartridge design as shown in Figure 6. It involves the use of two-walled ampoules which provide two levels of containment of the sample materials. BAC will evaluate the cartridge for mechanical strength and for its ability to provide the appropriate thermal environment within the prototype flight furnace. UAH will study crystal growth in the two-walled cartridge using the BAC #1 furnace.

Ground Science Furnace Development

UAH and BAC are working together to improve the ground science furnace. Later this year BAC will build and deliver a rotatable test stand so that convection studies can be carried out. BAC will also provide a programmable ampoule drive mechanism and a multizone heater system to facilitate future studies.

Presentations and Publications

1. Jason M. Kinser, Growth of Zinc Selenide Crystals by an Open Ampoule Method, Masters Thesis, The University of Alabama in Huntsville, 1987.

2. Jason M. Kinser, Elmer E. Anderson and M. K. Wu, "Growth of Zinc Selenide by Vapor Transport in an Open Ampoule," Bull. Amer. Phys. Soc. 32, 610 (1987). Paper presented at the NY APS Meeting, March 1987.

3. Jason M. Kinser, "Growth of ZnSe by Vapor Transport in an Open Ampoule." Paper presented at the March 1987 meeting of the Alabama Academy of Sciences, Florence, Alabama.

4. Hai-Yuin Cheng, Elmer E. Anderson and M. K. Wu, "Growth of ZnSe by Physical Vapor Transport," Bull. Amer. Phys. Soc. 32, 610 (1987). Paper presented at the NY APS meeting, March 1987.

References

1. Oliver, D. S. and W. R. Buchan, IEEE Trans. Electron Devices ED-18, 769 (1971).

2. Allen, J. W., A. W. Livingstone and K. Turvey, Solid State Electron. 15, 1363 (1972).

3. Ozsan, M. E. and J. Woods, Appl. Phys. Letters 25, 489 (1974).

4. Ozsan, M. E. and J. Woods, Solid State Electron. 18, 519 (1975).

5. Ozsan, M. E. and J. Woods, J. Phys. D 10, 1335 (1977).

6. Lawther, C. and J. Woods, phys. stat. solidi 50a, 491 (1978).

Figure 1. Small crystals of ZnSe. Magnification: upper photo x 48, lower photo x 10.

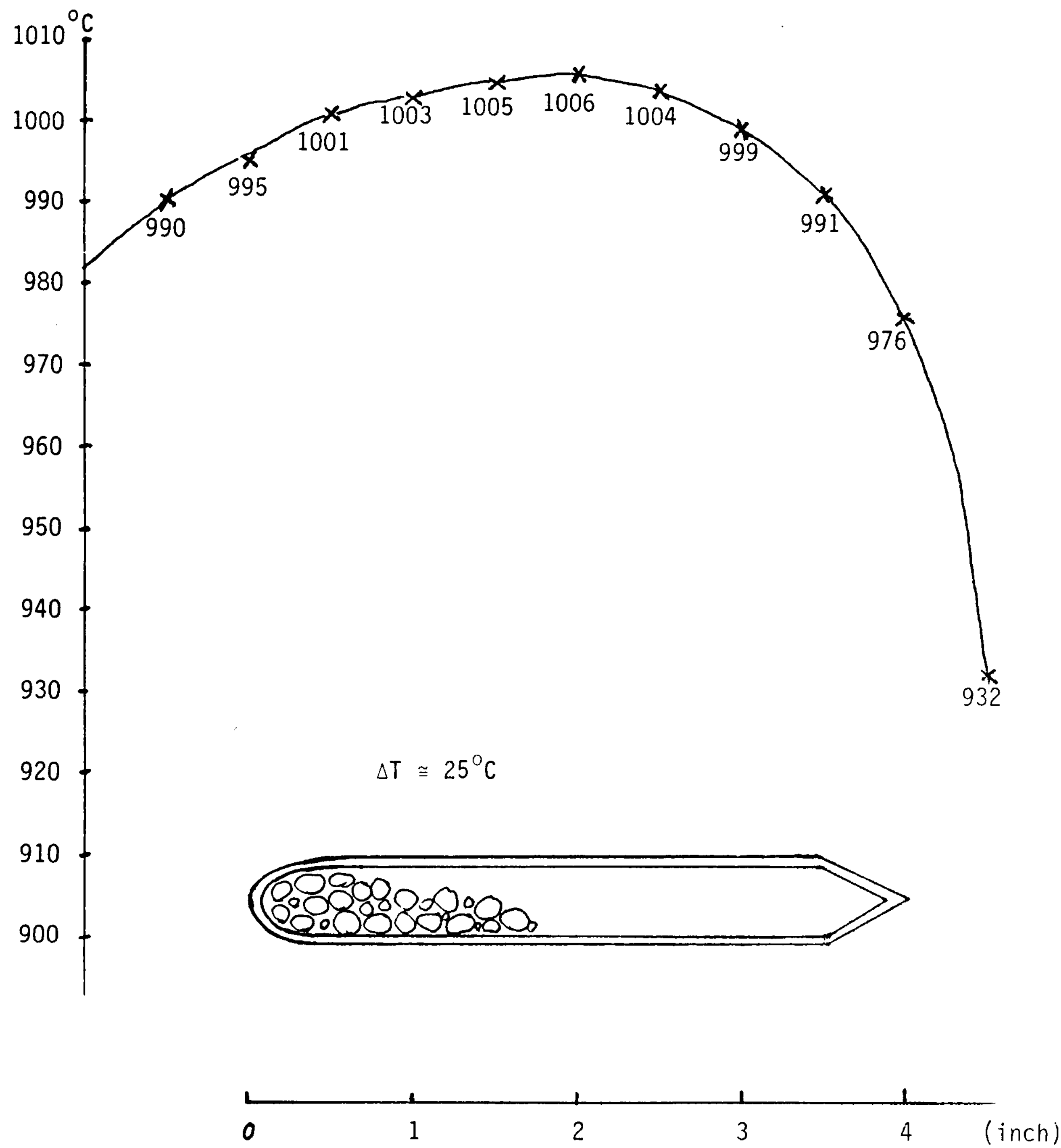

Fig. 2. Marshall Furnace Temperature Profile and Growth Position

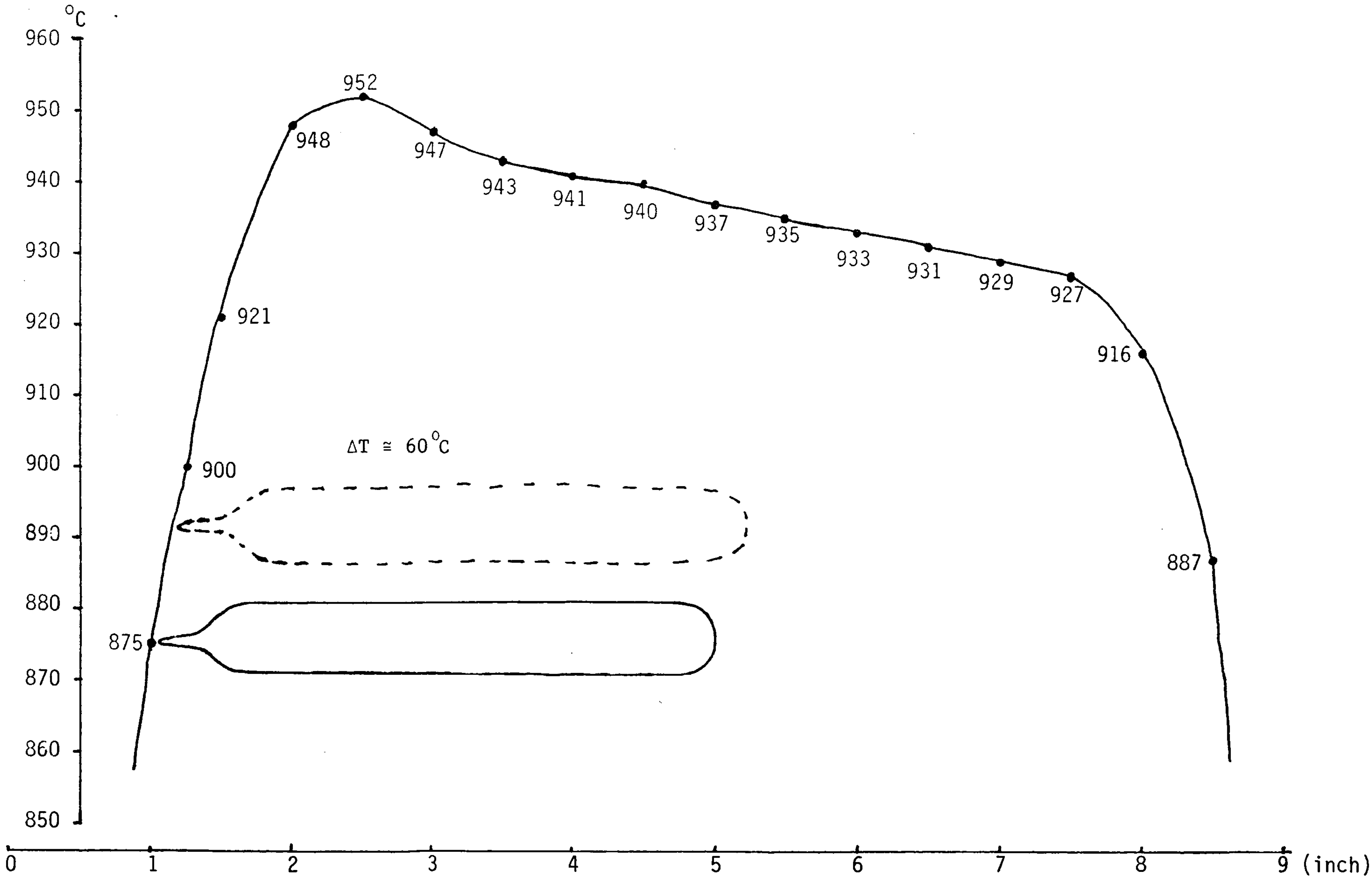

Fig. 3. Boeing #0 Furnace Temperature Profile and Growth Position

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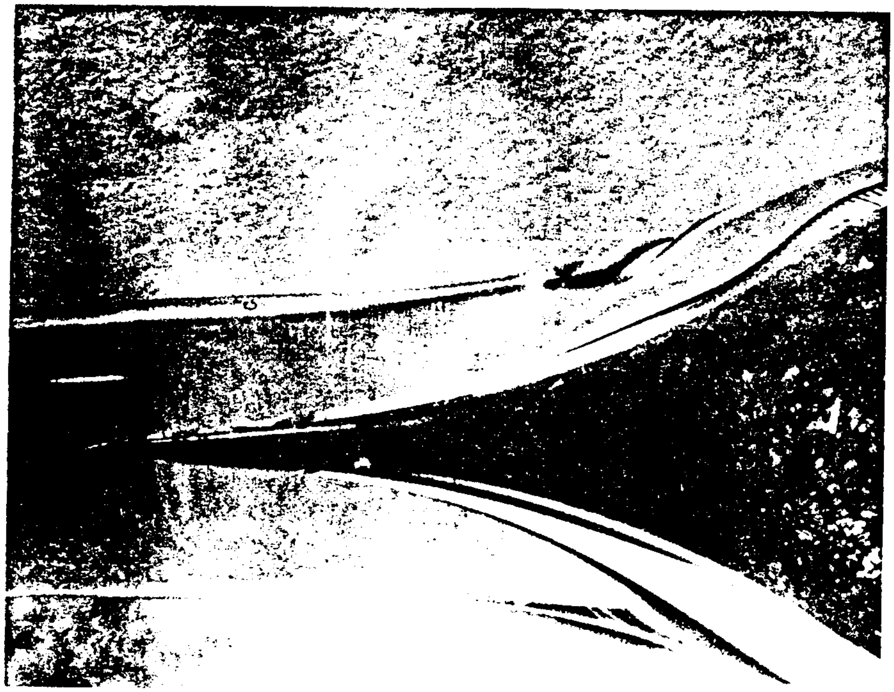

Fig. 4. Growth channel in the cold finger.
Magnification: x 6.3.

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Cartridge Baseline Design

BOEING

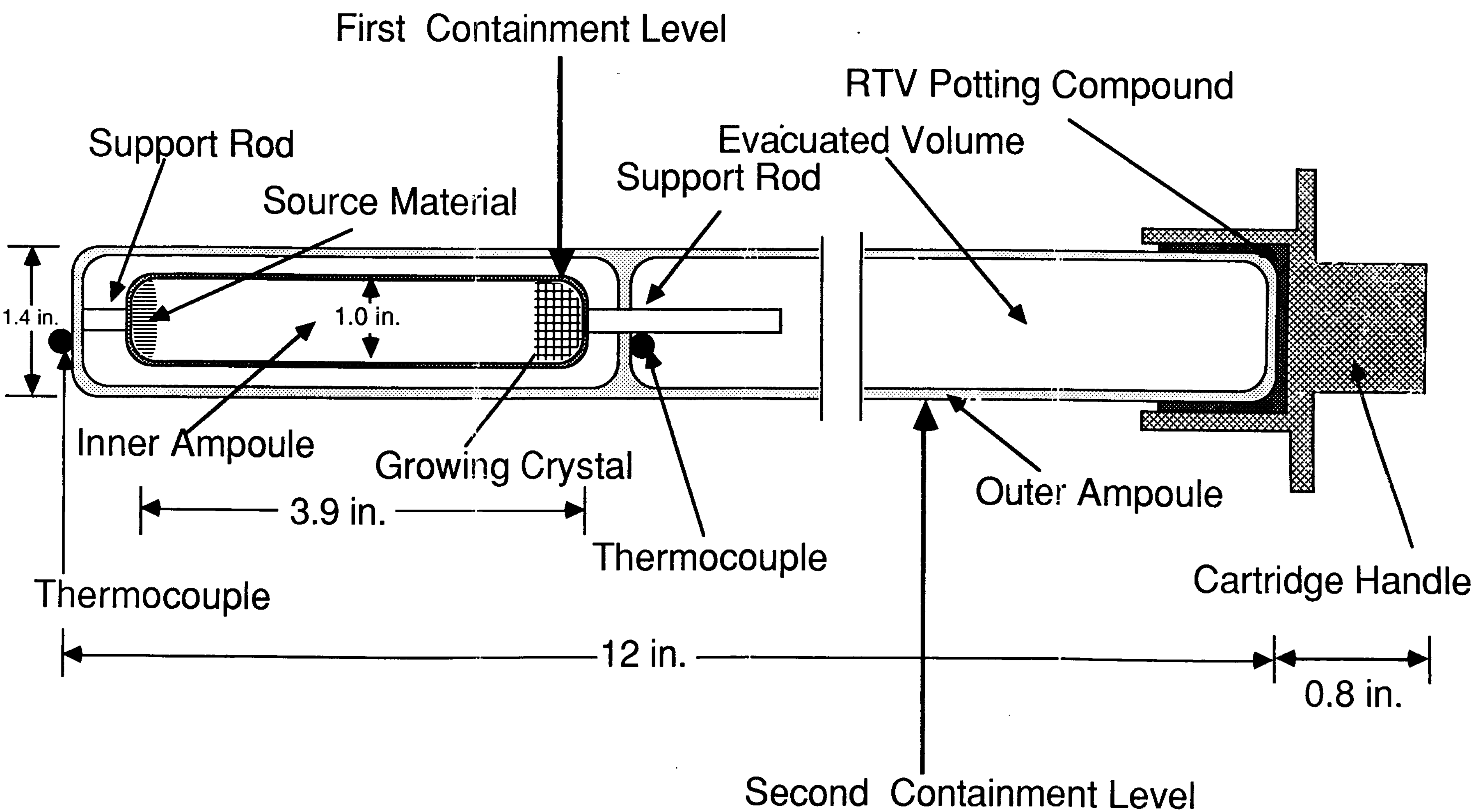

Fig. 6. Boeing Cartridge Baseline Design